Caustic Soda

Sodium Hydroxide (Caustic Soda), NaOH:

- Sodium hydroxide, NaOH, is a soft, waxy, white, corrosive solid.
- It is commonly known as lye or caustic soda.
- It is one of the important chemicals and is manufactured on a very large scale forming an important chemical industry.
- It is most conveniently manufactured by one of the following processes:
    1. Methods involving sodium carbonate as a starting material.
    2. Methods involving sodium chloride as starting material.

- **Methods involving sodium carbonate as a starting material**:
- Two methods are used. These are

(i) **Causticisation process (Gossage process)**:

$$Na_2CO_3 + Ca(OH)_2 \rightleftarrows CaCO_3 + 2NaOH$$

- The temperature is maintained 80-90°C by blowing steam. Caustic soda solution is drained out and evaporated to dryness when flakes of caustic soda are obtained.
- The most suitable concentration of sodium carbonate taken in this process is 15-20%.
- The caustic soda produced by this method is not pure and contains some calcium carbonate, sodium carbonate and calcium hydroxide as impurities.

(ii) **Lowig's process:**

$$Na_2CO_3 + Fe_2O_3 \rightarrow 2NaFeO_2 + CO_2$$
$$2NaFeO_2 + H_2O \rightarrow 2NaOH + Fe_2O_3$$

- The solution is filtered and evaporated to dryness to get flakes of sodium hydroxide.

- **Methods involving sodium chloride as starting material:**

Methods used are electrolytic as the electrolysis of sodium chloride solution is carried out in an electrolytic cell.

Principle: A sodium chloride solution contains Na^+, H^+, Cl^- and OH^- ions.

$$NaCl \rightleftarrows Na^+ + Cl^-$$
$$H_2O \rightleftarrows H^+ + OH^-$$

- On passing electricity, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. The discharge potential of H^+ ions is less than Na^+ ions, thus hydrogen ions get discharged easily and hydrogen is liberated. Similarly, at anode Cl ions are easily discharged as their discharge potential is less than that of OH^- ions. Cl_2 gas is therefore, liberated at anode.
- The solution on electrolysis becomes richer in Na^+ and OH^- ions.
- Since, chlorine reacts with sodium hydroxide solution even in the cold forming sodium chloride and sodium hypochlorite, it is necessary that chlorine should not come in contact with sodium hydroxide during electrolysis:

$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

- To overcome this problem, the, anode is separated from the cathode in the electrolytic cell either by using a porous diaphragm or by using a mercury cathode. Four methods are used, these are:
    - (i) Porous diaphragm process (Nelson cell process)
    - (ii) Castner-Kellner cell
    - (iii) Solvay-Kellner cell
    - (iv) Diaphragm cell

Properties:

Physical Properties:

- It is a white crystalline solid. It has soapy touch.
- It is highly deliquescent.
- Its density is 2.13 g/mL and melting point 318.4°C.
- It is highly soluble in water. It is bitter in taste.
- It is corrosive in nature.
- Its solubility is comparatively less in alcohol.

Uses:

- Sodium hydroxide is among the top ten industrial chemicals. It is an important industrial chemical because it is an inexpensive base for the production of other sodium salts. It is a strong base, and this property is useful in many applications. It is used:
  - As a reagent in. the laboratory.
  - In refining of petroleum.
  - In the manufacture of soap.
  - In the manufacture of sodium metal.
  - In the manufacture of paper and rayon.
  - In the manufacture of dyes and drugs.
  - As an absorber of gases.
  - In the manufacture of sodium hypochlorite, sodium chlorate and sodium nitrite.
  - For mercerizing cotton.
  - In large quantities in the production of aluminium which depends on its reaction with the amphoteric aluminium hydroxide.

Sodium Thiosulphate(Hypo) $Na_2S_2O_3.5H_2O$

- It is the sodium salt of an unstable acid, thiosulphuric acid ($H_2S_2O_3$). It is also known as hypo. The following methods can be used for its preparation:

(i) It is obtained by boiling sodium sulphite solution with flowers of sulphur.

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

(ii) **Spring's reaction**: The mixture of sodium sulphite and sodium sulphide is treated with calculated quantity of iodine.

$$Na_2S + I_2 + Na_2SO_3 \rightarrow Na_2S_2O_3 + 2NaI$$

(iii) When the solution containing sodium carbonate and sodium sulphide is treated with sulphur dioxide, sodium thiosulphate is formed with evolution of carbon dioxide.

$$2Na_2S + Na_2CO_3 + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$$

(iv)
$$4S + 6NaOH \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$$

With excess of sulphur, sodium pentasulphide is formed

$$Na_2S + 4S \rightarrow Na_2S_5$$

(v)
$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$
$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

- **Properties**:
- It is a colourless crystalline solid consisting of 5 molecules of water as water of crystallisation.
- It has the formula, $Na_2S_2O_3 \cdot 5H_2O$.
- It is soluble in water.
- It melts at 48°C.
- **Action of heat**: It is efflorescent substance. The water molecules are completely lost when heated at 215°C.

$$Na_2S_2O_3 \cdot 5H_2O \rightarrow Na_2S_2O_3 + 5H_2O$$

- When strongly heated above 223°C, it decomposes forming sodium sulphate (salt cake) and sodium pentasulphide.

$$4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S_5$$

- **Reaction with acids**: Dilute acids decompose it with evolution of SO_2 and precipitation of sulphur.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$$
$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S + H_2O$$

- **Oxidation**: It is oxidised by iodine quantitatively.

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Sodium tetrathionate

- **Reducing action**: It is oxidised by chlorine and bromine water. Sulphur is precipitated.

$$Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$$

It reduces $FeCl_3$ to $FeCl_2$

$$2Na_2S_2O_3 + 2FeCl_3 \rightarrow Na_2S_4O_6 + 2FeC1_2 + 2NaCl$$

- **Reaction with AgN03**: A white precipitate of silver thiosulphate is obtained which changes to yellow, brown and finally black due to the formation of silver sulphide.

$$2AgNO_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$$
$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$$

- Reaction with silver halides: Halides form complexes with sodium thiosulphate. Silver bromide forms argentothiosulphate complex.

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Sodium argentothiosulphate

- Similar reactions are observed with AgCl and AgI.
- This property is utilised in photography for fixing the negative and positive of black and white photography. It removes undecomposed AgBr present on the film.
- **Reaction with copper sulphate:** Cuprous thiosulphate is formed which dissolves in excess of sodium thiosulphate to form a complex.

$$CuSO_4 + Na_2S_2O_3 \rightarrow CuS_2O_3 + Na_2SO_4$$

Cupric thiosulphate

$$2CuS_2O_3 + Na_2S_2O_3 \rightarrow Cu_2S_2O_3 + Na_2S_4O_6$$

Cuprou thiosulphate

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \rightarrow Na_4[Cu_6(S_2O_3)_5]$$

Sodium cuprothiosulphate

- **Uses**:
- As an antichlor to remove excess of chlorine from bleached fabrics.
- In the extraction of silver and gold.
- In photography as a fixing agent in the name of hypo.
- As a reagent in iodometric and iodimetric titrations for the estimation of iodine, $CuSO_4$, $K_2Cr_2O_7$, $KMnO_4$, Na_3AsO_3 etc.

References:

- Industrial Inorganic Chemistry by Karl Heinz Buchel Hans-Heinrich Moretto Peter Woditsch, Second Edition WILEY-VCH.
- A Textbook of Inorganic Chemistry by O. P. Tandon
- Principles of Inorganic Chemistry by Puri, Sharma and Kalia